HYDROGENATION OF CARBON DIOXIDE OVER A SUPPORTED RUTHENIUM CATALYST

by

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INTRODUCTION

The ever increasing demand for natural gas as a fuel and raw material has stimulated renewed efforts to find other ways of producing methane. With more and more evidence of an "energy crisis" upon us, alternative approaches such as catalytically synthesizing methane from hydrogen and carbon dioxide meet with more promise of development.

A fairly complete summary of the research on carbon dioxide methanation has been given by Emmett (5), and details of the carbon monoxide-hydrogen reactions by Kirk and Othmer (10). Recent studies on the reaction between hydrogen and carbon dioxide over a supported nickel catalyst have been conducted by Binder and White (1) and by Dew et al. (3). Hydrogenation of carbon monoxide over a nickel catalyst has also been investigated (6). A few years ago, Karn and his associates (9) studied ruthenium as a possible methanation catalyst. In a recent experiment, Lunde and Kester (13) studied the reaction rates of methane production from hydrogen and carbon dioxide. The work described here is an extension of this effort, and presents the kinetics and possible mechanisms for the reaction between hydrogen and carbon dioxide.

It is believed by many workers (5) that carbon monoxide is a critical intermediate in carbon dioxide methanation. The following reactions summarize the overall reduction process.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad 1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad 2)$$

Because the equilibrium for Equation 1 is somewhat unfavorable at the reaction temperatures (200°-400° C), it can be argued that this reaction path is somewhat unlikely. A way out of this difficulty is to require that at these temperatures the methanation of carbon monoxide (Reaction 2) proceeds much faster than carbon monoxide production (Reaction 1). Reaction 2 could be in equilibrium. If carbon monoxide were rapidly consumed as it formed, no carbon monoxide would be observed in the reactor exit stream. This was the case with the data treated here (13). However, in his work with a ruthenium catalyst, Karn (9) did observe 1.5-2% carbon monoxide in the exit stream. The reason for his observation

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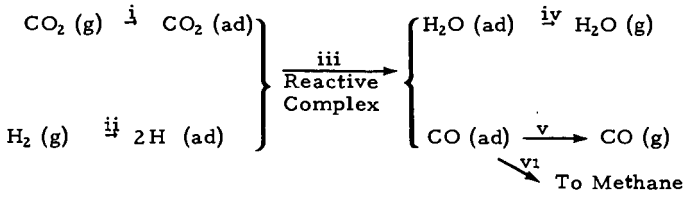
is not clear. It is possible that because of the extended operation (80 days) the catalyst may have become deactivated for the reaction converting carbon monoxide to methane.

REACTION MECHANISMS

Mechanism I

The reaction mechanism outlined here follows the work of Oki and Mezaki (14, 15) for the water-gas-shift reaction over iron oxide.



The absorbed carbon monoxide is ultimately reduced to methane by some reaction path not examined here. For the rate model developed in the next section, the reaction of 2H(ad) and CO(ad)(step iii) is assumed to offer the controlling resistance. The other reactions are assumed to be in equilibrium.

Mechanism II

An alternative mechanism, first suggested by Doehlemann (4) in 1938 and subsequently by Kul'kova and his coworkers (11, 12), has been described by Wagner (17). The catalyst was also iron oxide; however, the reaction temperatures were much higher (870°-1122°C) than in Oki and Mezaki's work (400°-450°C) and higher than in these data (207°-371°C) on ruthenium. This mechanism is included because it displays the observed dependence on both hydrogen and carbon dioxide, each to the first power (Table 2); it does not contain the hydrogen adsorption constant in its expression (which was found to be very small or zero); and it does not require the presence of three active sites indicated in Mechanism I(which may be somewhat improbable). The alternative mechanism (17) is –

$$CO_2\ (g) \overset{i}{\rightleftharpoons} CO_2\ (ad)$$

$$CO_2\ (ad) \xrightarrow{iib} CO\ (ad) + O(ad)$$

Adsorbed oxygen atoms react with molecular hydrogen in a single step:

$$H_2\ (g) + O(ad) \xrightarrow{iiib} H_2O\ (ad)$$

$$H_2O\ (ad) \xrightarrow{iv} H_2O\ (g)$$

$$CO\ (ad) \xrightarrow{v} CO\ (g)$$

$$CO\ (ad) \xrightarrow{vi} \text{To Methane}$$

This mechanism assumes that step iiib is rate-controlling and that the other steps are in equilibrium. *

RATE EQUATIONS

The model follows Hougen and Watson (7, 8) and employs a Langmuir-Hinshelwood rate model for Mechanism I. The modifications necessary for Mechanism II are given in the footnote below.

Assuming reaction step iii , Mechanism I, as rate-controlling, and with i, ii , iv, v, and vi in equilibrium, the following rate expression can be written:

$$r = k_F \theta^2_H \theta_{CO_2} \qquad 3)$$

where r is the forward reaction rate, k_F is the forward reaction rate coefficient, and θ_i represents the fraction of catalyst surface coverage of the i^{th} species.

The surface concentrations in equilibrium with the gaseous reactants or products can be represented by –

$$\theta^2_H = K_{H_2} P_{H_2} \theta^2_V \qquad 4)$$

$$\theta_{CO_2} = K_{CO_2} P_{CO_2} \theta_V \qquad 5)$$

$$\theta_{H_2O} = K_{H_2O} P_{H_2O} \theta_V \qquad 6)$$

$$\theta_{CO} = K_{CO} P_{CO} \theta_V \qquad 7)$$

where θ_V is the fraction of vacant catalyst surface, P_i is the equilibrium partial pressure, and K_i is the equilibrium absorption constant of the i^{th} species.

Inserting relationships 4 and 5 into Equation 3 gives –

$$r = k \theta^3_V P_{H_2} P_{CO_2} \qquad 8)$$

where

$$k = k_F K_{H_2} K_{CO_2} \qquad 9)$$

The total fraction surface coverage is equal to the sum of all occupied and unoccupied sites, which equals unity –

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*Mechanism II would modify the rate expression by reducing the exponent in the denominator of Equation 14 (presented later) to one and also eliminate $P_{H_2}^{1/2} K_{H_2}^{1/2}$ from the denominator of this expression.

$$1 = \theta_V + \theta_H + \theta_{CO_2} + \theta_{CO} + \theta_{H_2O} \qquad 10)$$

On inserting Equations 4, 5, 6, and 7 into Equation 10, one obtains –

$$1 = \theta_V + P_{H_2}^{1/2} K_{H_2}^{1/2} \theta_V + P_{CO_2} K_{CO_2} \theta_V + P_{CO} K_{CO} \theta_V + P_{H_2O} K_{H_2O} \theta_V \qquad 11)$$

which, on solving for θ_V^3, yields –

$$\theta_V^3 = 1/[1 + P_{H_2}^{1/2} K_{H_2}^{1/2} + P_{CO_2} K_{CO_2} + P_{CO} K_{CO} + P_{H_2O} K_{H_2O}]^3 \qquad 12)$$

Given the Arrhenius relationship

$$k = Ae^{-Ea/RT} \qquad 13)$$

and upon inserting Equations 12 and 13 into Equation 8, the final relationship obtained for correlation with the experimental data is –

$$r = Ae^{-Ea/RT} \frac{P_{H_2} P_{CO_2}}{[1 + P_{H_2}^{1/2} K_{H_2}^{1/2} + P_{CO_2} K_{CO_2} + P_{CO} K_{CO} + P_{H_2O} K_{H_2O}]^3} \qquad 14)$$

where*

r = reaction rate = $-\frac{dP_{CO_2}}{dt}$

A = pre-exponential factor

Ea = activation energy, cal/mole

R = 1.987 cal/deg-mole

T = degrees Kelvin

To evaluate this equation and to determine unknown constants, Equation 14 was rearranged as follows –

$$Y \equiv \ln \frac{r}{\frac{[1 + K_{H_2}^{1/2} P_{H_2}^{1/2} + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O}]^3}{P_{H_2} P_{CO_2}}} \qquad 15)$$

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* Other constants are the same as defined earlier.

where –

$$Y \equiv \ln A - \frac{Ea}{R}\left(\frac{1}{T}\right) \qquad (16)$$

After Y has been evaluated, the rate expression is then of the form $Y = mX + b$, so that a plot of Y versus $1/T$ for several runs forms a line with a slope $-Ea/R$ and a $1/T = 0$ intercept of lnk. If the correlation is good, the plot will show minimum scatter and good linearity when a proper form the rate equation has been chosen or a proper value of an adsorption coefficient has been obtained. A least squares calculation of a number of data points will give σ, the standard deviation.

The 62 data points shown in Table 1 contained experimental information on space velocity, average methane partial pressure (P_{CH_4}), average water vapor partial pressure (P_{H_2O}), and reactor temperature (T). The equilibrium carbon monoxide partial pressure, P_{CO}, was obtained from –

$$P_{CO} = \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^3 K_2} \qquad (17)$$

using average experimental partial pressures and K_2, the equilibrium constant for Reaction 2. The value K_2 was calculated as equal to exp $(1/1.987)(0.00266T + 23095.T^{-1} - 17688.T^{-2} + 17.600 - 6.744\ln T)$ from data contained in Reference 16.

The experimental reaction rate, r, was calculated as –

$$r = S_v (P_{CO_{2_{in}}} - P_{CO_{2\ out}}) \qquad (18)$$

where –

S_v is the experimental space velocity,

$P_{CO_{2_{in}}}$ is the partial pressure of CO_2 at the reactor inlet, and

$P_{CO_{2\ out}}$ is the partial pressure of CO_2 at the reactor outlet.

DISCUSSION

Determination of Form of Rate Equations

The minimum least squares standard deviation, σ, was taken as a quantitative measure of a fit of the data when correlating various forms of the driving force portion of the rate equation. Adsorption coeffients are treated below. The rate data treated are summarized in Table 1.

Table 1. SUMMARY OF EXPERIMENTAL TEST POINTS
(Data from Reference 13)

TEST NUMBER	REACTOR TEMP. (DEG F)	REACTOR TEMP (DEG C)	PCO2 CONSUMED (ATM/HR)	SPACE VELOCITY (1/HR)	INLET FLOW (CFH)	INLET CO2 (ATM)	OUTLET CO2 (ATM)	INLET H2 (ATM)	OUTLET H2 (ATM)	INLET H2O (ATM)	OUTLET H2O (ATM)	INLET CH4 (ATM)	OUTLET CH4 (ATM)
519.00	404.	207.	16.380	2854.	0.2117	0.2036	0.2002	0.0033	0.7894	0.0	0.0115	0.0	0.0038
520.00	433.	223.	32.730	3005.	0.2117	0.1978	0.1911	0.0091	0.7828	0.0	0.0220	0.0	0.0110
520.10	433.	223.	25.810	5565.	0.4172	0.2047	0.2015	0.8022	0.7893	0.0	0.0107	0.0	0.0054
521.00	443.	228.	38.510	5649.	0.4169	0.2034	0.1993	0.8035	0.7870	0.0	0.0137	0.0	0.0069
521.40	469.	243.	67.830	6175.	0.4239	0.2036	0.1970	0.8034	0.7767	0.0	0.0222	0.0	0.0111
522.30	505.	263.	141.000	6337.	0.4243	0.2055	0.1899	0.8050	0.7422	0.0	0.0453	0.0	0.0226
523.30	500.	260.	105.500	5828.	0.4256	0.1714	0.1575	0.6814	0.6257	0.1060	0.1454	0.0517	0.0744
524.00	527.	275.	127.400	5801.	0.4231	0.1790	0.1645	0.6818	0.6224	0.0987	0.1480	0.0475	0.0720
525.00	552.	289.	199.600	5874.	0.4231	0.1759	0.1573	0.6826	0.5896	0.0968	0.1739	0.0476	0.0381
525.10	545.	285.	175.500	5835.	0.4231	0.1799	0.1600	0.6800	0.5979	0.0994	0.1675	0.0476	0.0316
526.00	553.	289.	115.200	5319.	0.4231	0.1487	0.1331	0.5370	0.4721	0.2141	0.2678	0.1071	0.1340
527.00	576.	302.	157.000	5357.	0.4231	0.1485	0.1272	0.5298	0.4409	0.2197	0.2932	0.1090	0.1497
527.10	559.	293.	123.500	5300.	0.4231	0.1485	0.1318	0.5298	0.4595	0.2197	0.2773	0.1090	0.1380
527.20	569.	298.	142.500	5334.	0.4231	0.1485	0.1291	0.5298	0.4490	0.2197	0.2865	0.1090	0.1424
528.10	600.	316.	218.200	5426.	0.4227	0.1477	0.1181	0.5305	0.4071	0.2197	0.3217	0.1090	0.1606
529.20	598.	314.	171.000	5125.	0.4223	0.1243	0.0983	0.4362	0.3280	0.2965	0.3859	0.1499	0.1948
530.70	623.	328.	222.800	5150.	0.4223	0.1255	0.0916	0.4295	0.2878	0.3004	0.4178	0.1516	0.2097
531.00	652.	344.	252.600	5235.	0.4223	0.1229	0.0846	0.4202	0.2598	0.3059	0.4380	0.1579	0.2265
532.00	652.	344.	64.010	4660.	0.4223	0.0714	0.0594	0.1805	0.1498	0.5023	0.5441	0.2526	0.2733
539.50	423.	217.	26.910	4956.	0.4063	0.3415	0.3374	0.6654	0.6463	0.0	0.0109	0.0	0.0054
540.10	430.	221.	29.730	4967.	0.4063	0.3435	0.3393	0.6633	0.6427	0.0	0.0120	0.0	0.0060
540.20	440.	227.	36.660	5016.	0.4063	0.3435	0.3388	0.6633	0.6392	0.0	0.0147	0.0	0.0073
540.80	450.	232.	46.630	5062.	0.4063	0.3435	0.3382	0.6633	0.6340	0.0	0.0185	0.0	0.0093
541.10	485.	252.	86.020	5192.	0.4063	0.3455	0.3379	0.6613	0.6117	0.0	0.0336	0.0	0.0168
541.10	485.	252.	85.250	5192.	0.4063	0.3455	0.3380	0.6613	0.6121	0.0	0.0333	0.0	0.0166
542.00	490.	254.	85.980	5276.	0.4070	0.3434	0.3359	0.6634	0.6146	0.0	0.0330	0.0	0.0165
542.10	505.	263.	123.300	5324.	0.4070	0.3434	0.3336	0.6634	0.5955	0.0	0.0472	0.0	0.0236
543.00	495.	257.	55.830	4741.	0.4070	0.3305	0.3264	0.5117	0.4762	0.1051	0.1314	0.0595	0.0728
544.00	512.	267.	96.920	4782.	0.4070	0.3312	0.3241	0.5124	0.4567	0.1081	0.1539	0.0552	0.0761
544.10	520.	271.	103.900	4815.	0.4070	0.3312	0.3236	0.5124	0.4466	0.1081	0.1578	0.0552	0.0796
544.20	528.	276.	141.600	4818.	0.4070	0.3312	0.3208	0.5124	0.4221	0.1081	0.1752	0.0552	0.0868
544.30	534.	279.	150.100	4839.	0.4070	0.3312	0.3202	0.5124	0.4170	0.1081	0.1790	0.0552	0.0907
545.00	519.	271.	85.050	4577.	0.4070	0.3302	0.3226	0.4476	0.3872	0.1543	0.1973	0.0782	0.0997
545.10	528.	276.	93.110	4624.	0.4073	0.3302	0.3220	0.4476	0.3822	0.1543	0.2010	0.0782	0.1016
545.30	534.	279.	107.400	4626.	0.4070	0.3302	0.3209	0.4476	0.3722	0.1543	0.2085	0.0782	0.1053
546.10	541.	283.	121.500	4668.	0.4078	0.3276	0.3182	0.4427	0.3593	0.1587	0.2206	0.0779	0.1088
547.00	572.	300.	194.800	4726.	0.4070	0.3275	0.3125	0.4428	0.3086	0.1583	0.2578	0.0783	0.1286
548.00	560.	293.	56.320	4177.	0.4070	0.2647	0.2581	0.1527	0.1021	0.3941	0.4320	0.2024	0.2215
549.00	587.	308.	69.570	4276.	0.4070	0.2647	0.2568	0.1526	0.0914	0.3941	0.4400	0.2024	0.2259
549.10	590.	310.	133.500	4404.	0.4070	0.2865	0.2729	0.2477	0.1379	0.3164	0.3996	0.1632	0.2085
550.00	616.	324.	167.500	4497.	0.4070	0.2855	0.2686	0.2502	0.1146	0.3154	0.4167	0.1627	0.2137
551.00	640.	338.	196.500	4560.	0.4066	0.2855	0.2659	0.2494	0.0916	0.3161	0.4342	0.1627	0.2221
560.00	624.	329.	629.500	5483.	0.4067	0.3417	0.2998	0.6686	0.3220	0.0	0.2590	0.0	0.1295
561.00	610.	321.	363.200	4939.	0.4067	0.3237	0.2943	0.4848	0.2412	0.1375	0.3184	0.0863	0.1503
562.00	602.	317.	270.100	4721.	0.4059	0.3151	0.2923	0.4142	0.2214	0.1865	0.3302	0.0944	0.1664
563.00	596.	313.	210.000	4587.	0.4059	0.3017	0.2824	0.3468	0.1880	0.2400	0.3587	0.1217	0.1813
564.00	588.	309.	131.100	4361.	0.4059	0.2855	0.2721	0.2362	0.1268	0.3214	0.4031	0.1638	0.2048
565.00	588.	309.	131.900	4566.	0.4321	0.1708	0.1509	0.3028	0.2014	0.3542	0.4340	0.1803	0.2204
567.00	598.	314.	277.800	5022.	0.4321	0.2143	0.1800	0.4990	0.3213	0.1981	0.3372	0.0988	0.1684
568.00	601.	316.	346.000	5234.	0.4321	0.2258	0.1860	0.5672	0.3622	0.1456	0.3066	0.0717	0.1521
569.00	617.	325.	618.700	5872.	0.4321	0.2600	0.2027	0.7482	0.4515	0.0	0.2351	0.0	0.1175
570.00	531.	277.	201.900	5670.	0.4311	0.2623	0.2436	0.7514	0.6561	0.0	0.0737	0.0	0.0368
571.00	527.	275.	122.000	4971.	0.4311	0.2226	0.2078	0.5567	0.4820	0.1567	0.2142	0.0776	0.1063
572.00	526.	274.	88.950	4932.	0.4311	0.2011	0.1887	0.5043	0.4459	0.2052	0.2479	0.1030	0.1244
573.00	519.	271.	80.190	4552.	0.4311	0.1924	0.1807	0.4154	0.3571	0.2692	0.3136	0.1307	0.1589
575.00	524.	273.	46.150	4231.	0.4311	0.1604	0.1523	0.2654	0.2203	0.3895	0.4186	0.1984	0.2131
576.00	527.	275.	62.320	4347.	0.4082	0.2828	0.2755	0.2692	0.2179	0.3063	0.3430	0.1554	0.1738
577.00	528.	276.	73.800	4581.	0.4082	0.3000	0.2923	0.3700	0.3153	0.2288	0.2681	0.1149	0.1345
578.00	529.	276.	90.360	4754.	0.4082	0.3089	0.3003	0.4350	0.3728	0.1806	0.2255	0.0892	0.1116
579.00	529.	276.	144.500	5058.	0.4082	0.3223	0.3106	0.5442	0.4566	0.0993	0.1634	0.0478	0.0798
580.00	530.	277.	151.000	5382.	0.4082	0.3306	0.3195	0.6270	0.5453	0.0386	0.0983	0.0175	0.0473
581.00	531.	277.	184.600	5644.	0.4558	0.3377	0.3253	0.6760	0.5837	0.0	0.0675	0.0	0.0337

Since some of the data were collected at moderate to high conversions, an initial screening was conducted on all runs to determine if any were close to the thermodynamic limit. Two runs were found to be closer than 5% (Runs 533 and 534 in Ref. 13) of the thermodynamic limit and were not included in the final treatment. This means that any influence by the reverse reaction, Equation 1, on the rate data was no greater than 5% and for most runs was much less than 1%.

If one assumed that the adsorption of hydrogen is rate-controlling (reaction path i), then σ is found to be equal to 0.3305 (Table 2); if the absorption of carbon dioxide is assumed to be controlling (reaction path ii), σ is 0.4688. It appears that assuming hydrogen to be in equilibrium is consistent with Bond (2), who has summarized the activation energies and pre-exponential factors for hydrogen reactions on various transition metals. Bond indicates an activation energy for hydrogen adsorption generally around 5 kcal and never greater than 10.6 kcal. It appears that a lower activation energy than was observed for these data (18.33 kcal) is necessary for the adsorption of hydrogen onto active metal sites to be controlling. Bond also tabulates pre-exponential factors that would indicate reaction rates much faster than observed for these data.

Secondly, the adsorption of carbon dioxide was not considered to be rate-controlling, as the resulting rate equation would not reflect the preferred dependence on the rate on P_{H_2} to the first power (Table 2). Oki and Mezaki (14) also considered the possibility of only one adsorbed hydrogen atom reacting with one adsorbed carbon dioxide molecule. This would reflect a dependence of P_{H_2} to the one-half power with P_{CO_2} to the first power in the rate equation. This relationship, when correlated with the data, yields an unsatisfactorily high standard deviation of 0.3165.

The most significant improvement and the best correlation of the data with the driving force expression were obtained with a dependence of $P_{H_2}P_{CO_2}$ (both to the first power) giving a σ of 0.2113. This expression suggests a rate-controlling reaction of two adsorbed hydrogen atoms with one adsorbed carbon dioxide molecule (Mechanism I) or the reaction of gaseous hydrogen with an adsorbed oxygen atom (Mechanism II).

Determination of Adsorption Coefficients

With this form of the rate expression, further least squares calculations were performed to evaluate the various adsorption constants. A constant such as K_{CO_2} would be systematically varied on a trial-and-error basis until a minimum was obtained in the σ versus K_{CO_2} curve (Figure 1). The other adsorption constants were also evaluated in this manner. The minimum values for the adsorption constants are given in Table 3. Minimum values were obtained for all reaction gases except hydrogen. The σ versus K_{H_2} curve (not shown) was quite broad and shallow in the region of K_{H_2} below 10^{-3} atm^{-1}. Apparently these experimental data are not of sufficient quality to obtain a precise value of K_{H_2}, which is therefore reported to be less than 10^{-3} atm^{-1} for this temperature range. No temperature dependence of the adsorption constants was included in the evaluation.

Table 2. FIT OF RATE EQUATION TO EXPERIMENT DATA

Form of Rate Equation*	Least Squares Standard Deviation, σ
Driving Force Evaluation	
P_{H_2}	0.3305
P_{CO_2}	0.4688
$P_{H_2}^{1/2}$	0.3708
$P_{H_2}^{1/2} P_{CO_2}$	0.3165
$P_{H_2} P_{CO_2}$	0.2113
Adsorption Coefficient Evaluation	
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2}]}$	0.1818
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO} P_{CO_2}]^2}$	0.1795
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2}]^3}$	0.1294
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2} + K_{CO} P_{CO}]^3}$	0.1157
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O}]^3}$	0.1144
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2} + K_{CO} P_{CO}]}$	0.1680
$\frac{P_{H_2} P_{CO_2}}{[1 + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O}]}$	0.1650

* Driving force and adsorption terms only

Table 3. EVALUATION OF ADSORPTION CONSTANTS FOR 1/2% RUTHENIUM ON ALUMINA*

Adsorption Constant	Experimental Value, atm^{-1}
MECHANISM I	
K_{CO_2}	0.760
K_{H_2}	$<10^{-3}$
K_{CO}	475
K_{H_2O}	0.160
MECHANISM II	
K_{CO_2}	2.62
K_{H_2}	$< 10^{-3}$
K_{CO}	1490
K_{H_2O}	0.491

* Determined by the least squares trial-error fit of the 62 data points over a temperature range of 207°-358°C. These are average constants for this temperature range.

For Mechanism I, the various adsorption constants included in Equation 15, the least squares calculation for the 62 data points, gave a correlation of σ = 1144. The resulting curve is shown in Figure 2. The activation energy was found to be 18.33 kcal/mole, and the pre-exponential factor was 3.524×10^{10} atm^{-1} hr^{-1}.

For Mechanism II, the values were slightly different, with $A = 1.037 \times 10^{10}$ atm^{-1} hr^{-1}, and Ea = 17.90 kcal/mole.

CONCLUSION

Literature data on the rates of carbon dioxide methanation collected over a 1/2% ruthenium-on-alumina catalyst at 1 atmosphere and temperatures from 207° to 371°C have been interpreted to proceed stepwise first to carbon monoxide and ultimately to methane. Correlation of the data yielded a dependence on P_{H_2} and P_{CO_2}, both to the first power. Two possible mechanisms consistent with previous literature studies have been suggested and discussed. Rate constants, activation energies, and adsorption constants were determined.

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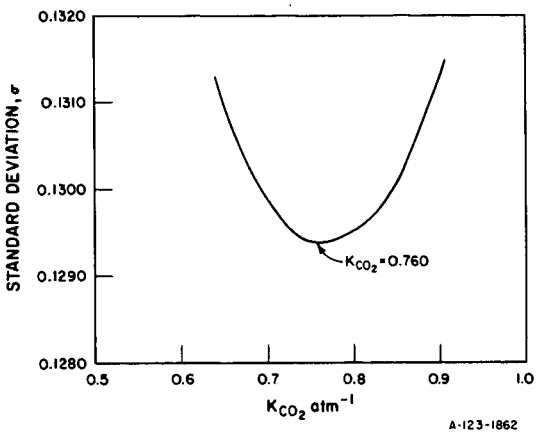

Figure 1. DETERMINATION OF CO_2 ADSORPTION CONSTANT USING EQUATION 15, MECHANISM I

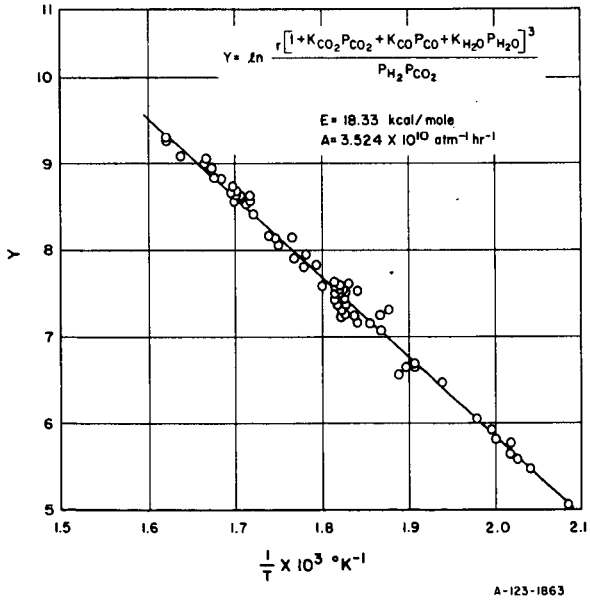

Figure 2. ACTIVATION-ENERGY PLOT OF 62 DATA POINTS